

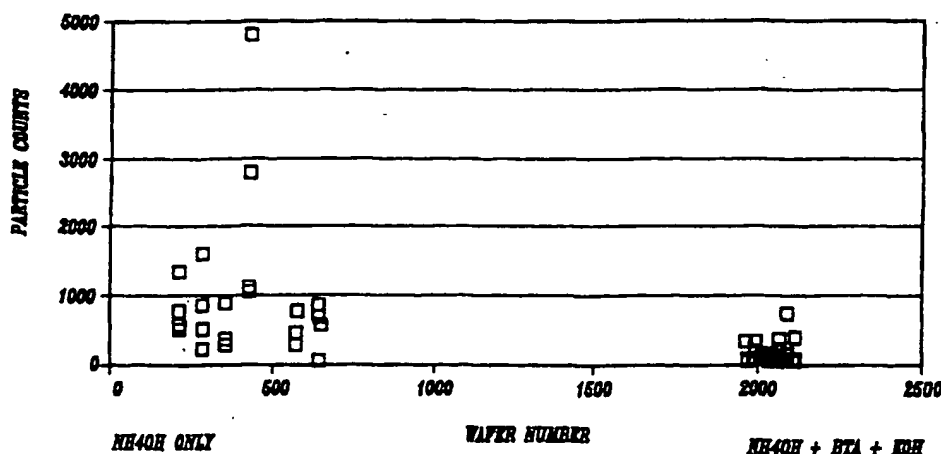
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(54) Title: **METHODS AND CLEANING SOLUTIONS FOR POST-CHEMICAL MECHANICAL POLISHING**

## (57) Abstract

In accordance with the present invention, methods and compositions are provided for the effective removal of copper by-products from the surface of semiconductor wafers following CMP. The present invention comprises a solution of a volatile copper chelating agent, an organic copper corrosion inhibitor, and a water-soluble, metal hydroxide for cleaning and processing semiconductor wafers. The present invention further comprises a method for cleaning scrub brushes and wafers, and prolonging the life of mechanized scrub brushes following CMP of semiconductor wafers using the solution of the present invention.



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## METHODS AND CLEANING SOLUTIONS FOR POST-CHEMICAL MECHANICAL POLISHING



## METHODS AND SOLUTIONS FOR POST-CHEMICAL MECHANICAL POLISHING

### Field of the Invention

The present invention relates to chemical mechanical polishing (hereinafter  
5 "CMP") in the fabrication of semiconductor wafers for integrated circuits. More  
specifically, the present invention relates to methods and compositions for removal of  
by-products formed during copper-CMP from the semiconductor wafers' surface and  
to methods for reducing the accumulation of these by-products on scrub brushes used  
in a post-CMP Cleaner. Copper by-products can also be cleaned following other  
10 processes such as CVD, annealing, and plasma etch.

### Background of the Invention

CMP is often used in the fabrication of integrated circuits to planarize a  
surface of a semiconductor wafer to facilitate subsequent photolithographic process  
steps or to globally remove portions of wafer layers that were laid down during the  
15 construction of multi-level interconnection structures. In particular, CMP can be  
used in fabricating inter-layer interconnects (e.g., metal plugs for contacts or vias), or  
for forming intra-layer interconnects (e.g., copper interconnect lines in a damascene  
process). In addition, CMP can be used in dual damascene processes in which both  
inter-layer and intra-layer interconnects are formed by deposition of a single metal  
20 layer that fills etched vias and trenches in dielectric layers. A subsequent CMP  
process is done to remove the metal above the dielectric layer leaving the metal in the  
trenches and vias.

Of the several techniques for planarizing the surface of a semiconductor  
wafer, CMP is now considered the most effective method available for planarizing

wafers with submicron lines. During the CMP process, a wafer is mounted on a rotary carrier or chuck, with the integrated circuit side of the wafer facing outward. A polishing pad is then brought into contact with the side of the wafer having the integrated circuit thereon. Pressure may be applied by the carrier and/or the polishing pad to effectuate polishing of the wafer. In some CMP machines, the wafer rotates while the polishing pad remains stationary, in others, the pad rotates while the wafer carrier remains stationary. And in yet other types of CMP machines, both the wafer carrier and the polishing pad rotate simultaneously. The polishing pad is generally presoaked and continually re-wetted with a slurry that has a variety of abrasive particles suspended in a solution to aid in the polishing process. Typically, the abrasive particles range in size from 30 to 1,100 nanometers.

In addition, a CMP polishing slurry for removing metal may also contain a suitable oxidizing agent that chemically facilitates removal of materials from the wafer surface. The selection of the oxidizing agent present in a CMP slurry typically depends upon the chemical composition of the material that is preferentially being removed from the wafer surface. Thus, protruding areas on an uneven semiconductor wafer surface are removed by the combined effects of mechanical abrasion and chemical action, while the recessed regions are protected by a passivation and/or inhibition layer. After the polishing process is complete, the wafers go through a post-CMP cleanup to remove residual slurry, slurry particles, particles formed in the material removal process, and other potential contaminants from the planarized wafer surface.

Copper is an attractive interconnecting material in integrated circuit manufacturing due to its low resistivity. Reducing the resistance of interconnects is important in order to achieve high speeds by decreasing the RC delay as the size of the structures shrink to quarter micron or less. Copper and copper alloys are promising candidates for the next generation of semiconductor microelectronic devices if patterning and manufacturing problems can be solved. One of the problems with using copper is its susceptibility to corrosion and the difficulty of removing metallic and particle by-products that adhere to the surface of semiconductor wafers subjected to copper-CMP.

Polishing slurries currently used for planarization in the semiconductor industry are typically aqueous suspensions of an abrasive (such as alumina, ceria, or zirconia), an organic dispersant, and a suitable oxidizing agent. The abrasive material is generally Alumina or silica. The organic dispersant is usually a weak

organic acid such as citric acid or weak base such as amine. And, the oxidizing agent works to oxidize the metal surface. Surface oxidation allows higher copper removal rates and facilitates planarization. Some oxidizing agents employed in commercially available or proprietary slurries are metal compounds that are present in significant concentrations. For example, ferric nitride has been used as an active and stable oxidizing agent to polish copper. Other metal-based chemicals may be added to slurries to improve dispersion or otherwise enhance CMP performance. As a result, a significant amount of these metal impurities remain on the wafer after polishing and normal cleaning. These impurities must then be removed from the surface of the planarized wafer.

The typical cleaning process performed on wafers after CMP processing consists of scrubbing the wafer with a 2% solution of ammonium hydroxide or ammonium hydroxide mixed with hydrogen peroxide. This scrubbing process is generally performed more than once. This is a reasonably effective cleaning process for removing particulate matter accumulated from the polishing slurry, and it does significantly reduce the ionic and organic contaminants adhering to the wafer. However, these conventional cleaning agents will attack the copper surface, which will result in etching and corrosion of the copper lines in the wafers. The invented solution can be used to clean any patterned or unpatterned wafer with which has copper in its composition, including semiconductor wafers or other semiconductor substrates such as those with or without active devices or circuitry, and partially processed wafers, as well as silicon on insulator, hybrid assemblies, flat panel displays, Micro Electro-Mechanical Sensors (MEMS), MEMS wafers, hard computer disks or other materials that would benefit from planarization.

For example, as disclosed by Schonauer et al. (U.S. Patent No. 5,662,769), ammonium hydroxide solutions are not always adequate to remove metal contaminants from the surface of a wafer. In particular, Schonauer et al. reported that when iron-containing slurries are used in the process of polishing wafers, and subsequently scrubbed with 2% ammonium hydroxide, a very high level of Fe and Fe-containing contaminants are bound at the wafer surface. Schonauer et al. teaches that these iron contaminants can be effectively removed from the wafer surface by cleaning the wafer with a pH stable solution composed of a chelating agent selected from citrates and EDTA, and hydrofluoric acid (HF).

Shiramizu (U.S. Patent No. 5,509,970) teaches a method of cleaning semiconductor silicon wafers using an aqueous acid solution. Shiramizu discloses

use of a solution of hydrogen fluoride to strip metallic films from the surface of semiconductor substrates. The stripped metallic film is then released into the aqueous cleaning solution, where the metallic particles are chelated by the action of ammonia or EDTA.

5           Although the above described prior art methods and solutions are somewhat effective at removing post-CMP by-products from wafer surfaces, there are significant drawbacks associated with use of these prior art solutions. For example, both hydrofluoric acid and ammonium hydroxide, commonly used in conventional post-CMP cleaning processes, are well known to cause etching and corrosion of  
10 metal surfaces. Furthermore, seepage of cleaning solutions can occur through defects in a wafer dielectric layer. Voids which exist in the copper layer will be corroded by any trapped chemical at elevated temperatures. This would happen frequently in semiconductor processing such as those temperatures used following the oxide deposition step.

15           Winebarger et al. (U.S. Patent No. 5,478,436) suggest that one solution to the seepage and metal corrosion problem is to select chemical constituents of wafer cleaning solutions so that even if the chemicals diffuse into interconnect regions, they will not react with the metallurgical compounds present. Winebarger et al. teach that one such cleaning solution includes an organic solvent and a compound containing  
20 fluorine, such as hydrogen fluoride, perfluoric acid, and the like. The preferred cleaning solution described by Winebarger et al. comprises a solution containing about 80% by weight ethylene glycol, about 10% by weight ammonium fluoride, about 5% by weight water, and about 1% by weight surfactant. Some problems with the Winebarger et al. cleaning solution include the cost associated with using high  
25 concentrations of ethylene glycol, safety considerations in utilizing large amounts of organic solvents, and the fact that the ethylene glycol-based cleaning solution must also be cleaned from the semiconductor wafer surface in a subsequent cleaning step. In addition, it has been observed that ammonium fluoride is absorbed over the silica surface. This results in delayed crystallization and time-dependent defectivity levels.

30           Another known way to reduce corrosion of metal surfaces and seepage of corrosive chemicals to interconnect surfaces during chemical cleaning is to add benzotriazole (BTA) to the wafer cleaning solution. BTA and other triazole-based compounds are film-forming materials that serve to cover the metal or metal oxide surface of a wafer, thereby providing protection against corrosive elements present in  
35 an aqueous cleaning system. The thickness and density of the protective film

depends upon the concentration of BTA and the time of exposure of the wafer to BTA. Although BTA is an effective protective agent, there are drawbacks associated with inclusion of BTA in the cleaning process. In particular, in effective concentrations, BTA tends to form a layer on the surface of the wafer that is so thick and dense that later removal of the protective coating, as required for downstream wafer manufacturing steps, is problematic.

An example of a post-CMP cleaning solution that includes BTA is provided in McGrath et al. (U.S. Patent No. 5,244,539). McGrath et al. describe compositions and methods for stripping metallic films from printed circuit boards. The compositions described by McGrath et al. dissolve tin-copper alloys and also include benzotriazole to reduce corrosion of copper surfaces on the circuit boards. The McGrath et al. cleaning solution is composed of: an aqueous solution of nitric acid; a source of ferric ions; a source of halide ions; and, a source of ammonium ions in an amount sufficient in combination with the halide ions to solubilize the tin, substantially eliminate sludge formation in the cleaning solution bath, reduce attack on the copper substrate, and provide a bright copper finish after solder removal.

Luo et al. (Electrochemical Society Proceedings, 97-31: 73-83 (1998)) describes acidic CMP solutions that are specifically designed for use with semiconductor wafers containing copper interconnect layers. These copper-CMP solutions are composed of alumina particles as the abrasive,  $\text{Fe}(\text{NO}_3)_3$  as the chemical etchant, and BTA as an inhibitor of copper corrosion. Luo et al. show that if BTA is present in the CMP solution, even in small concentrations, the polishing and chemical removal rate of copper is dramatically decreased due to the presence of a protective film that formed by BTA. While Luo et al. propose a CMP composition that is optimal for copper-CMP, they do not describe any methods or compositions for the post-CMP removal of copper particles from the surface of semiconductor wafers.

The CMP process and the post-CMP cleaning process are normally part of a mechanized operation, during which appropriate polishing and cleaning solutions are injected onto the wafer surface as it moves through the manufacturing procedure. Generally, semiconductor wafers are manufactured using multi-platen semiconductor wafer production tools that integrate CMP processing with immediate post-CMP wafer cleaning. Wafer processing machines, such as the AVANTGAARD 776 (IPEC Planar, Phoenix, AZ), perform CMP on semiconductor wafers in conjunction with an AVANTI 7700 (IPEC Planar, Phoenix, AZ) wafer cleaning module,

contained within the same piece of equipment. The AVANTI 7700 integrated cleaner provides post-polish cleaning and drying of processed wafers. Each scrub station consists of two double-sided pancake brush scrubbing stations in series and a spin rinse/dry station with an integrated megasonic spray arm. The results of the mechanical cleaning action of the scrub station are further enhanced by introduction of post-CMP cleaning solutions directly to the wafer's surface. Integration of CMP and post-CMP processes in one instrument minimizes oxidation of wafer surfaces following CMP and reduces airborne contamination.

Use of an integrated semiconductor wafer CMP machine requires selection of an effective post-CMP cleaning solution. Use of improper post-CMP solutions may result in rapid accumulation of residue on wafer scrub brushes. The presence of this residue on post-CMP brushes clogs the brushes and causes a rapid fall-off in cleaning efficacy. Poor cleaning results in semiconductor wafers containing an unacceptably high number of surface contaminants that may interfere with subsequent integrated circuit manufacturing steps. The contaminate and particulate matter left on the wafer after copper-CMP, and on the brush in cleaning, contains trace amounts of metal commonly found in slurry plus larger amounts of copper containing by-products from the CMP process.

Known prior art post-CMP cleaning solutions are ill-suited for removing contaminants following CMP of semiconductor wafers containing copper interconnect lines or wafers that otherwise have accumulated particles and contaminants. Use of prior art post-CMP cleaning solutions results in rapid build up of residues on wafer scrub brushes and ineffective removal of particles from wafer surfaces. In order to obtain acceptably clean wafer surfaces following post-CMP cleaning with prior art formulations, wafer scrub brushes must be changed frequently. However, this causes a slow down in wafer throughput and increases production expenses due to the replacement costs of post-CMP scrub brushes. Therefore, what is needed in the art is an effective post-CMP wafer processing solution that is able to remove particles and other contaminants from semiconductor wafer surfaces without causing excessive corrosion while preventing build-up of residue on the surface of post-CMP scrub brushes.

#### Summary of the Invention

In accordance with the present invention, methods and compositions are provided for the effective removal of by-products from the surface of semiconductor wafers following CMP of copper damascene semiconductor wafers. During the CMP



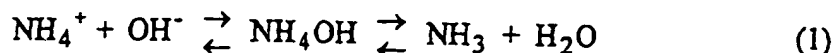
process, semiconductor wafers accumulate surface particles that must be removed by post-CMP cleaning. Cleaning is achieved through the use of scrub brushes which sweep the semiconductor wafer surface under light pressure and the application of cleaning compositions. Use of the post-CMP compositions of the present invention prevent semiconductor wafer scrub brushes from accumulating residue that clogs the brushes, thereby resulting in diminished removal of contaminants and particles from the surface of the semiconductor wafers and necessitating frequent scrub brush replacement. Thus, use of the post-CMP solutions of the present invention also reduces downtime of expensive CMP manufacturing tools and reduces the expense of frequently replacing clogged and ineffective wafer scrub brushes.

The post-CMP semiconductor wafer cleaning solutions of the present invention comprise: (1)  $\text{NH}_4\text{OH}$ ; (2) an organic copper corrosion inhibitor, such as benzotriazole; and, (3) a water-soluble metal dioxide such as  $\text{KOH}$ ,  $\text{NaOH}$ ,  $\text{RbOH}$ ,  $\text{Ca}(\text{OH})_2$ , or  $\text{CsOH}$ ; and deionized water. In one preferred embodiment, the inventive composition is used as a pre-mixed wafer cleaning solution, preferably having the following components:  $\text{NH}_4\text{OH}$ , BTA,  $\text{KOH}$  and deionized water. The inventive composition may also be delivered to the semiconductor wafer surface directly through the scrub brush tool as disclosed in Gill (U.S. Patent No. 5,144,711), which is hereby fully incorporated by reference.

The methods and compositions of the present invention provide for enhanced removal of unwanted particles and by-products from the CMP of semiconductor wafer surfaces that contain copper and further prevent the accumulation of residue on the wafer scrub brushes, thereby extending the useful life of the post-CMP scrub brushes. The mechanisms of action of the solutions of the present invention is explained below:

Ammonium hydroxide solutions are effective cleaners of copper residue from semiconductor wafer CMP scrub brushes by the production of ammonia ( $\text{NH}_3$ ), which is a volatile copper chelating agent. However, concentrations of ammonium hydroxide that are effective for copper particle removal also cause corrosion of metal surfaces present on processed semiconductor wafers due to the production of  $\text{NH}_4^+$  ions. To protect these metallic surfaces, BTA, a corrosion inhibitor, is added to the post-CMP solutions of the present invention. To further inhibit the corrosive activity of  $\text{NH}_4\text{OH}$  solutions, a water-soluble, metal hydroxide solution is also added to the post-CMP solutions. The presence of  $\text{OH}^-$  ions, from the water-soluble metal hydroxide solution in the cleaning solution, shifts the equilibrium of products formed

from aqueous  $\text{NH}_4\text{OH}$ , in favor of greater production of  $\text{NH}_3$ , the desired copper chelating molecule. The disassociation products of ammonium hydroxide in aqueous solution are represented in equation (1).



5        In prior art post-CMP solutions that contained ammonium hydroxide and BTA, both  $\text{NH}_4$  and  $\text{NH}_3$  ions are formed. However, in the inventive post-CMP solutions, the addition of an appropriate water soluble metal hydroxide solution increases the overall concentration of  $\text{OH}^-$  ions in the solution. This shifts the  
10        equilibrium of the neutral disassociation of  $\text{NH}_4\text{OH}$  to the right, thus increasing the level of the desired copper chelating agent,  $\text{NH}_3$ .

      Thus, inclusion of an alkaline metal base in the inventive post-CMP solution allows a lower concentration of  $\text{NH}_4\text{OH}$  to be used which results in reduced etching. As a result, a lower BTA concentration is needed, thus eliminating the polymerization of BTA over the copper surface. BTA inhibits corrosion by  
15        stimulating the production of a surface protective layer on wafer surfaces. The higher the BTA concentration, the thicker and denser the protective layer becomes on wafer surfaces, making later removal of the protective surface for subsequent steps in manufacturing of integrated circuits more problematic. Therefore, one major  
20        advantage of the inventive post-CMP solution is that it allows usage of a lower BTA concentration during post-CMP cleaning of semiconductor wafers to remove copper particles. This results in deposition of a BTA protective film that is thinner and less dense than that deposited by prior art solutions. Nonetheless, the inventive post-CMP solution contains enough BTA to still be effective at preventing corrosion to the metallic surfaces of semiconductor wafers exposed to the inventive solution.  
25        Furthermore, the production of a thinner, less dense protective layer allows a significant decrease in the polishing time and the amount of abrasive materials that are required to achieve later removal of the BTA protective film from CMP processed semiconductor wafers.

      Wafer CMP is typically performed in an integrated machine that combines  
30        CMP steps with post-CMP cleaning and drying processes to produce a planarized semiconductor wafer. The methods and solutions of the present invention are suitable for use in integrated CMP machines. Typically a post-CMP cleaning system may include a work surface with dual CMP scrub brushes, a wafer transfer mechanism, fluid dispensers, spin-rinse-dry unit, and a controller. The solutions of

the present invention are injected into the machine during the cleaning process, as follows: the controller is configured to cause the post-CMP system to perform a first cleaning of a CMP processed semiconductor wafer. The semiconductor wafer is moved into a first cleaning chamber, where the wafer is subjected to a first cleaning  
5 with the inventive post-CMP solution and a second cleaning with deionized water. The wafer is then moved to a second cleaning chamber and again cleaned with the inventive composition and cleaned with deionized water under similar conditions, as described for the first cleaning chamber. The conditions of the first and second cleaning need not be the same. By use of the controller, an operator can  
10 independently control top and bottom brush velocity, brush pressure, and fluid delivery sequences and flows. The semiconductor wafer is then moved into a spin, rinse, dry unit in which there is a megasonic cleaner. Lastly, the CMP processed semiconductor wafer is removed dry from the CMP machine.

A primary objective of the invention is to provide an effective method and  
15 cleaning solution for the post-CMP removal of particles and resulting contaminants from the surface of a semiconductor wafers that have been subjected to copper-CMP. It is a further objective to provide an invention that prevents the buildup of CMP residue on the surfaces of post-CMP wafer scrub brushes used during post-CMP cleaning of semiconductor wafers. Yet another purpose of the invention is to provide  
20 a post-CMP solution that is effective at removal of particles from semiconductor wafers, but does not use high concentrations of highly corrosive chemicals. A final objective of the invention is to provide a post-CMP solutions that contains low concentrations of anti-corrosion triazole-based chemicals such as BTA, so as to prevent the buildup of too dense of a protective layer on the surface of post-CMP  
25 cleaned semiconductor wafers.

In summary, the present invention provides a copper by-product removal solution comprising ammonium hydroxide, an organic copper corrosion inhibitor, and a water-soluble, metal hydroxide solution. The present invention further presents methods for post-CMP cleaning of semiconductor wafers in post-CMP work stations  
30 such that post-CMP scrub brushes do not rapidly accumulate residue of copper by-products which cause a reduction in the efficacy of wafer cleaning.

#### Brief Description of the Drawings

The foregoing aspects and many of the attendant advantages of this invention will become more readily appreciated as the same becomes better understood by

reference to the following detailed description, when taken in conjunction with the accompanying drawings, wherein:

FIGURE 1 is a diagram illustrative of a conventional post-CMP brush and fluid cleaning system.

5        FIGURE 2 is a graph showing post-CMP particles present on semiconductor wafers after cleaning with one embodiment of the present invention as opposed to cleaning with a prior art post-CMP wash solution of  $\text{NH}_4\text{OH}$  only.

Detailed Description of the Preferred Embodiment

10        The post-CMP semiconductor wafer cleaning solutions of the present invention comprise: (1)  $\text{NH}_4\text{OH}$  or an equivalent copper chelating agent such as water, carbon monoxide, or formic acid which are less effective for copper than  $\text{NH}_3$ ; (2) an organic copper corrosion inhibitor, such as benzotriazole; (3) a water-soluble, metal hydroxide solution such as  $\text{KOH}$ ,  $\text{NaOH}$ ,  $\text{RbOH}$ ,  $\text{Ca}(\text{OH})_2$ , or  $\text{CsOH}$ ; and deionized water. In one preferred embodiment, the inventive composition is used as  
15        a pre-mixed wafer cleaning solution, preferably having the following components:  $\text{NH}_4\text{OH}$ , BTA, and  $\text{KOH}$  and deionized water. The inventive composition may also be delivered to the semiconductor wafer surface directly through the scrub brush tool as disclosed in Gill (U.S. Patent No. 5,144,711), which is hereby fully incorporated by reference.

20        Metal chelating agents are chemical compounds that can bind to metal ions yet maintain the complex metal in an aqueous state. During the removal of copper by-products from the surface of CMP processed wafers, effective chelating agents are those that bind metal ions tightly enough to prevent the metal ions from re-attaching themselves to the surface of the washed semiconductor wafer, or to the surface of the  
25        post-CMP scrub brushes that are used to enhance removal of CMP introduced surface contaminants. Possible chelating agents for use in post-CMP removal of metal ions are: ammonia, citrates, amino acids and EDTA. However, the inventive post-CMP solutions is composed of the volatile copper chelating agent, ammonia, because it does not leave behind a precipitate upon the wafer surface after the final  
30        wafer rinse and drying step. Therefore, ammonia ( $\text{NH}_3$ ) is the most preferred copper chelating agent in the practice of manufacturing semiconductor wafers because of its effectiveness and its highly volatile nature.

35        Preferably, the post-CMP solution of the present invention is made by dissolving ammonium hydroxide at a concentration range of the 0.01-2% (weight/weight) in deionized water. Most preferable, the inventive post-CMP

solution is made by dissolving ammonium hydroxide at a concentration of 0.28% (weight/weight) in deionized water.

The inventive post-CMP solution contains a water-soluble, highly disassociative alkaline metal, such as KOH, NaOH, RbOH,  $\text{Ca}(\text{OH})_2$ , or CsOH, in a concentration that is effective at shifting the equilibrium of disassociation of ammonium hydroxide from the production of both ammonia and ammonium ions in aqueous solution, to where ammonia ions are produced in vast excess over ammonium ions. In the practice of the invention, KOH is the preferred hydroxide metal because  $\text{Na}^+$  ions, produced from disassociation of NaOH, behave as small molecules and can diffuse very rapidly into cracks and other wafer faults thereby causing deterioration of oxide layers. Rubidium and Cesium hydroxide compounds will work in the present invention, but they are too expensive for commonplace wafer manufacturing purposes. Furthermore, Calcium Hydroxide is poorly soluble and does not allow a wide range of concentrations to be used. Calcium Hydroxide may also form poorly soluble complexes with copper-CMP by-products that will then precipitate over the wafer surface.

For clean room use, preferably, water-soluble, metal hydroxide solutions are present in the concentration range of 0.1-5% (weight/weight). More preferably, the inventive post-CMP solution contains KOH in a concentration range of 0.1-2% (weight/weight). Most preferably, the inventive post-CMP solution contains KOH at a concentration of 0.42% (weight/weight).

As delineated in U.S. Patent Nos. 5,772,919; 5,411,677; and 5,236,626, a wide variety of triazole derivatives are effective at protecting copper surfaces from corrosion. However, benzotriazole (BTA) has long been accepted in the semiconductor wafer manufacturing industry as the inhibitor of choice. Use of other triazole derived metal inhibitors in the inventive post-CMP solutions should be possible. However, the introduction of any of these chemicals into the semiconductor manufacturing clean rooms would require testing and time. In addition, some triazole compounds, such as, for example, butanotriazole, haxanotriazole, octanotriazole, and halotriazole are themselves corrosive, and therefore, are not preferred corrosion inhibitors even though they might work.

Preferably, the inventive post-CMP solution contains an organic corrosion inhibitor in a concentration range of 0.0001-1%. More preferably, the inventive post-CMP solution contains BTA in a concentration range of 0.0001-1% (weight/weight).

Most preferably, the inventive post-CMP solution contains BTA at a concentration of 0.0003% (weight/weight).

The inventive post-CMP solutions may contain the above identified components in a wide variety of possible ratios that nonetheless still fall within the individual concentration ranges previously set forth. Table 1 provides one example of a preferred post-CMP solution.

TABLE 1

	Compound	% by weight/weight
Chelating Agent	NH <sub>4</sub> OH	1.0
Alkaline Metal	KOH	2.0-1.5
Corrosion Inhibitor	BTA	0.2

Table 2 sets forth a more preferred post-CMP solution comprising:

TABLE 2

	Compound	% by weight/weight
Chelating Agent	NH <sub>4</sub> OH	0.1
Alkaline Metal	KOH	0.5
Corrosion Inhibitor	BTA	0.0001

Most preferably, the post-CMP solution has the formulation presented in Table 3.

TABLE 3

	Compound	% by weight/weight
Chelating Agent	NH <sub>4</sub> OH	0.28
Alkaline Metal	KOH	0.42
Corrosion Inhibitor	BTA	0.0003

The inventive post-CMP solutions can be used in a variety of ways to effectively remove copper-CMP generated metal particles from the surface of semiconductor wafers. The inventive solutions may be sprayed or otherwise introduced under pressure to the surface of contaminated wafers such that the metallic residue is cleaned away. Alternatively, CMP processed wafers may be

dipped or otherwise submerged into a bath composed of the inventive post-CMP solution. Preferably, some type of wafer scrub brush is used to further enhance surface removal of contaminating particles from wafers. The inventive post-CMP solution may be introduced to the surface of the semiconductor wafer using a flow-through scrub brush that is of a dual pancake brush design.

FIGURE 1 illustrates a post-CMP cleaning system, according to one embodiment of the present invention. The post-CMP cleaning system includes a work surface 12, wafer scrub brushes 14 and 16, fluid dispensing reservoirs 32 and 34, and a controller 36. This embodiment is implemented with a CMP machine such as, for example, an AVANTGAARD 776 CMP machine available from IPEC Planar, Phoenix, AZ. To clean semiconductor wafer 24, wafer heads 26 hold wafer 24 while a down force is applied to scrub brushes 14 and 16 to achieve a scrubbing pressure on the wafer surface. In addition, wafer scrub brushes 14 and 16 are removably secured to cleaning heads 21 and 23, respectively. Cleaning heads 21 and 23 are connected to tubular drive shafts 20 and 22. Shafts 20 and 22 have conduits 17 and 19 through which a cleaning fluid can flow. An opening 25 into the shaft 22 is provided in the flat face of cleaning head 23 which also has a plurality of channels 27 to distribute the post-CMP cleaning fluid across the surface of wafer scrub brush 16. A wafer scrub brush 16 is formed as a single piece of porous, elastic material with a substrate portion that has a surface abutting cleaning head 23. The scrub brush 16 has a plurality of cylindrical nubs 18 on the cleaning surface forming projections for scrubbing surfaces of semi-conductor wafers. Wafer scrub brushes 14 and 16 are rotated at rates of  $\omega_{SB_1}$  (100 to 300 rpm) and  $\omega_{SB_2}$  (100 to 200 rpm) respectively, while semiconductor wafer 24 is rotated by wafer heads 26. Preferably the top brush rotates faster than the bottom brush. Fluid dispensers 32 and 34 dispense the post-CMP cleaning solution to conduits 17 and 19 for distribution to the wafer scrub brushes 14 and 16. Fluid dispensers 32 and 34 are configured to store several different cleaning solutions and deionized (DI) water. Controller 36 includes one or more microprocessors or microcontrollers (not shown) that are suitably programmed to control the operation of motors 28 and 30 that independently rotate shafts 20 and 22, fluid flow from fluid dispensers 32 and 34, the cleaning brush pressure against wafer 24 and the rotation speed of wafer heads 26. Controller 36 includes a memory (not shown) to store software or firm ware programs that are executed to control the operation of post-CMP cleaning system.

The defects over the post Cu-CMP wafer are caused mainly by the deposition of by-products containing copper remaining on the wafer after processing.  $\text{NH}_3$  is a good chelating agent which enhances dissolution of by-products containing copper and allows for the removal of surface defects. BTA is normally included in slurry formulae to provide a protection layer for copper against corrosion. This protection layer may be damaged during end-phases of the polishing process. Therefore this protective layer must be restored. Addition of BTA is a good way to restore this protective layer.

KOH is added to enhance the chelating ability of the ammonia. By doing so, the concentration of ammonia can be reduced, thus minimizing its etching of the wafers copper features.

The effectiveness of the inventive post-CMP solutions were evaluated by quantitating the number of particle adders remaining on wafer surfaces after post-CMP cleaning. "Particle adders" are those particles that have been added to the wafer surface by the CMP process. As is well known in the art of semiconductor wafer fabrication, pre- and post-wafer surface scans can be performed to quantitate the number of particle adders. Semiconductor wafer surface scans can be performed using, for example, a Tencor 6420 Surfscan 6420 Unpatterned Surface Inspection System, as manufactured by KLA-Tencor, San Jose, CA.

To test various cleaning solutions for their efficacy at removing copper particle adders from the surface of semiconductor wafer discs, a set of contaminated semiconductor wafers were subjected to a variety of test conditions. Prior to CMP each test wafer was surface scanned to quantitate particle contamination. CMP was performed using copper containing semiconductor wafers. After CMP, each test wafer was moved into a first cleaning unit where for 20 seconds the experimental post-CMP cleaning mixture was sprayed onto the surface of the wafer at a flow rate of 100-150 milliliters per minute (ml/min). During this 20 second wash the top scrub brush was rotated at 220 revolutions per minute (rpm) with 0-1 pounds per square inch (psi) down force, while the bottom brush was rotated at 100 rpm. Each disc was then cleaned with DI water for five seconds under the same rpm and down force conditions as used with the experimental cleaning solution. Wafers were then moved to a second cleaning unit and cleaned again cleaned with the experimental post-CMP solution for 20 seconds, followed by 15 seconds of rinsing with DI water. Both of the cleaning processes performed in the second cleaning unit were performed using the same rpm and down force conditions as used in the first cleaning unit. Each



semiconductor wafer was then moved into a spin, rinse, dry unit (SRD) in which there is a megasonic cleaner. Discs are then removed dry from the unit and surface particles quantitated by a surface scan with the Tencor 6420 surface scanner.

FIGURE 2 presents particle data obtained from surface scans of semiconductor wafers subjected cleaning with only  $\text{NH}_4\text{OH}$  as compared to those cleaned with the post CMP cleaning solution comprising 0.28% ammonium hydroxide, 0.42% potassium hydroxide, and 0.0003% BTA. When 2% (weight-volume) ammonium hydroxide was used, significant surface particles and copper surface etching features were present after processing as few as 25 semiconductor wafers. By the time the wafer scrub brushes had cleaned 500 semiconductor wafers, surface particles had increased to almost 5,000 per wafer.

A post-CMP solution composed of 2% ammonium hydroxide and 0.01% BTA was somewhat better at reducing particle adders than ammonium hydroxide alone. However, after processing 25 wafers, particle adders again reached an unacceptable level, indicating the need to change wafer scrub brushes.

In contrast, use of one of the inventive post-CMP solutions, comprising 0.28% ammonium hydroxide, 0.42% potassium hydroxide, and 0.0003% BTA, results in post-CMP wafers that have significantly fewer surface particles than the wafers had prior to post -CMP cleaning with a 2% ammonium hydroxide solution. This is reflected by the substantially lower particle numbers shown in FIGURE 2. Furthermore, more than 600 wafers could be subjected to post-CMP cleaning before the wafer scrub brushes required replacement.

The embodiments of the post-CMP system described above are illustrative of the principles of the present invention and are not intended to limit the invention to the particular embodiments described. For example, in light of the present disclosure, those skilled in the art can devise, without undue experimentation, embodiments using wafer scrub brushes or post-CMP systems other than those described. In particular, non-rotating scrub brushes may be used rather than the rotating pancake brushes described. Further, other embodiments may employ three or more cleaning steps on a single semiconductor wafer to achieve desired levels of surface cleanliness. Accordingly, while the preferred embodiment of the invention has been illustrated and described, it will be appreciated that various changes can be made therein without departing from the spirit and scope of the invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A semiconductor wafer cleaning solution comprising water, ammonium hydroxide, a water-soluble metal hydroxide, and an organic corrosion inhibitor.
2. The semiconductor wafer cleaning solution of Claim 1 wherein the ammonium hydroxide is present in a concentration range of 0.01% to 2% weight/weight.
3. The semiconductor wafer cleaning solution of Claim 1 wherein the water soluble metal hydroxide is selected from the group consisting of KOH, NaOH, RbOH,  $\text{Ca}(\text{OH})_2$ , or CsOH.
4. The semiconductor wafer cleaning solution of Claim 3 wherein the water-soluble metal hydroxide is present in the concentration range of 0.1% to 5% (weight/weight).
5. The semiconductor wafer cleaning solution of Claim 1 wherein the organic corrosion inhibitor is a triazole compound selected from the group consisting of benzotriazole, butanotriazole, hexanotriazole, octanotriazole, and halotriazole.
6. The semiconductor wafer cleaning solution of Claim 5 wherein the triazole compound is present in the range of 0.0001% to 2% (weight/weight).
7. A method of cleaning semiconductor wafer surfaces during manufacturing causing the semiconductor wafer surface to come in contact with a semiconductor wafer cleaning solution comprising: water, ammonium hydroxide, a water-soluble metal hydroxide, and an organic corrosion inhibitor.
8. The method of Claim 7 wherein the ammonium hydroxide present in the semiconductor wafer cleaning solution is present in a concentration range of 0.01% to 2% weight/weight.

9. The method of Claim 7 wherein the water-soluble metal hydroxide in the semiconductor wafer cleaning solution is selected from the group consisting of KOH, NaOH, RbOH,  $\text{Ca}(\text{OH})_2$ , or CsOH.

10. The method of Claim 9 wherein the water-soluble metal hydroxide is present in the semiconductor wafer cleaning solution in the concentration range of 0.1% to 5% (weight/weight).

11. The method of Claim 7 wherein the organic corrosion inhibitor present in the semiconductor wafer cleaning solution is selected from the group consisting of benzotriazole, butanotriazole, hexanotriazole, octanotriazole, and halotriazole.

12. The method of Claim 11 wherein the organic corrosion inhibitor is present in the semiconductor wafer cleaning solution in a concentration range of 0.0001% to 2% (weight/weight).

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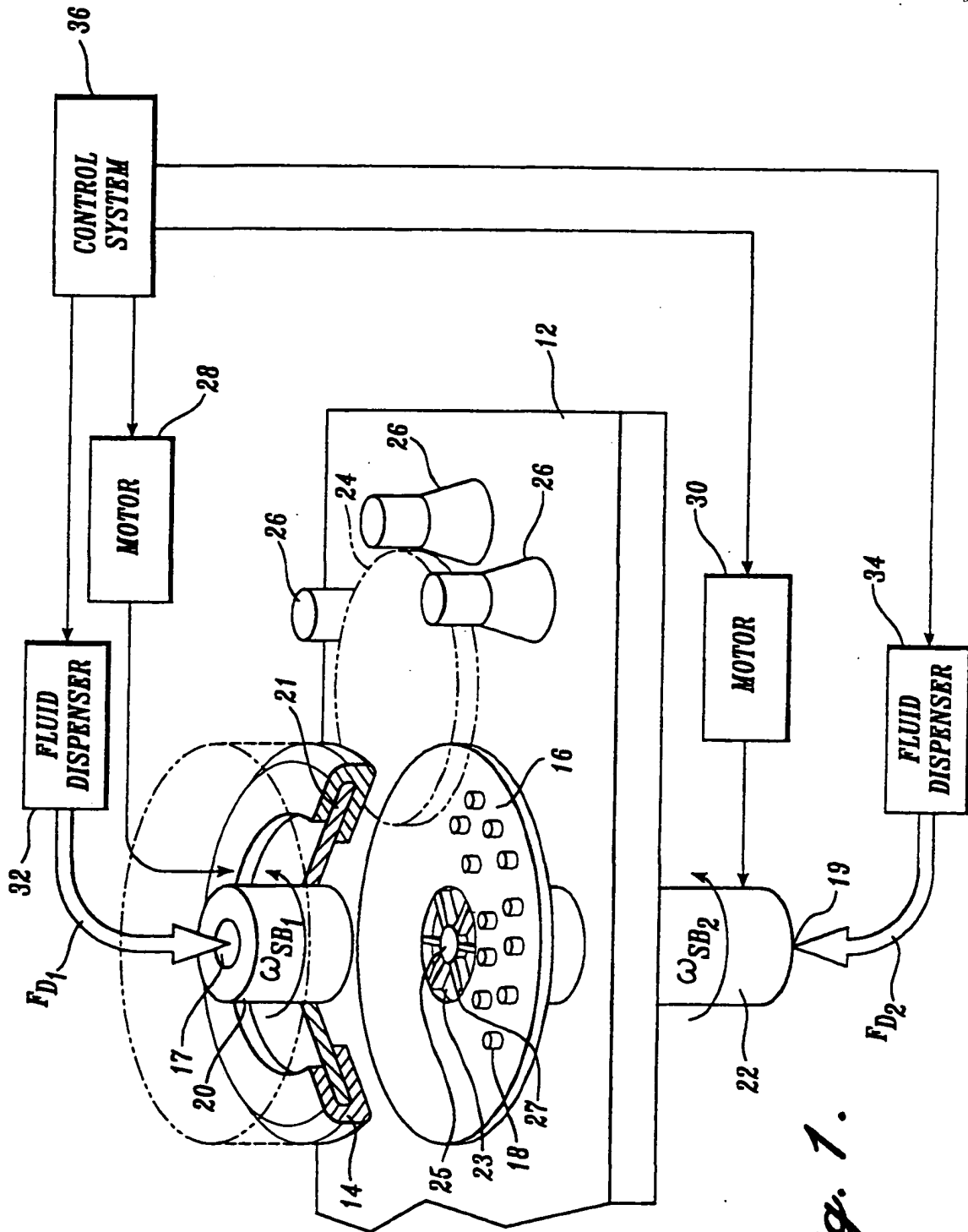


Fig. 1.

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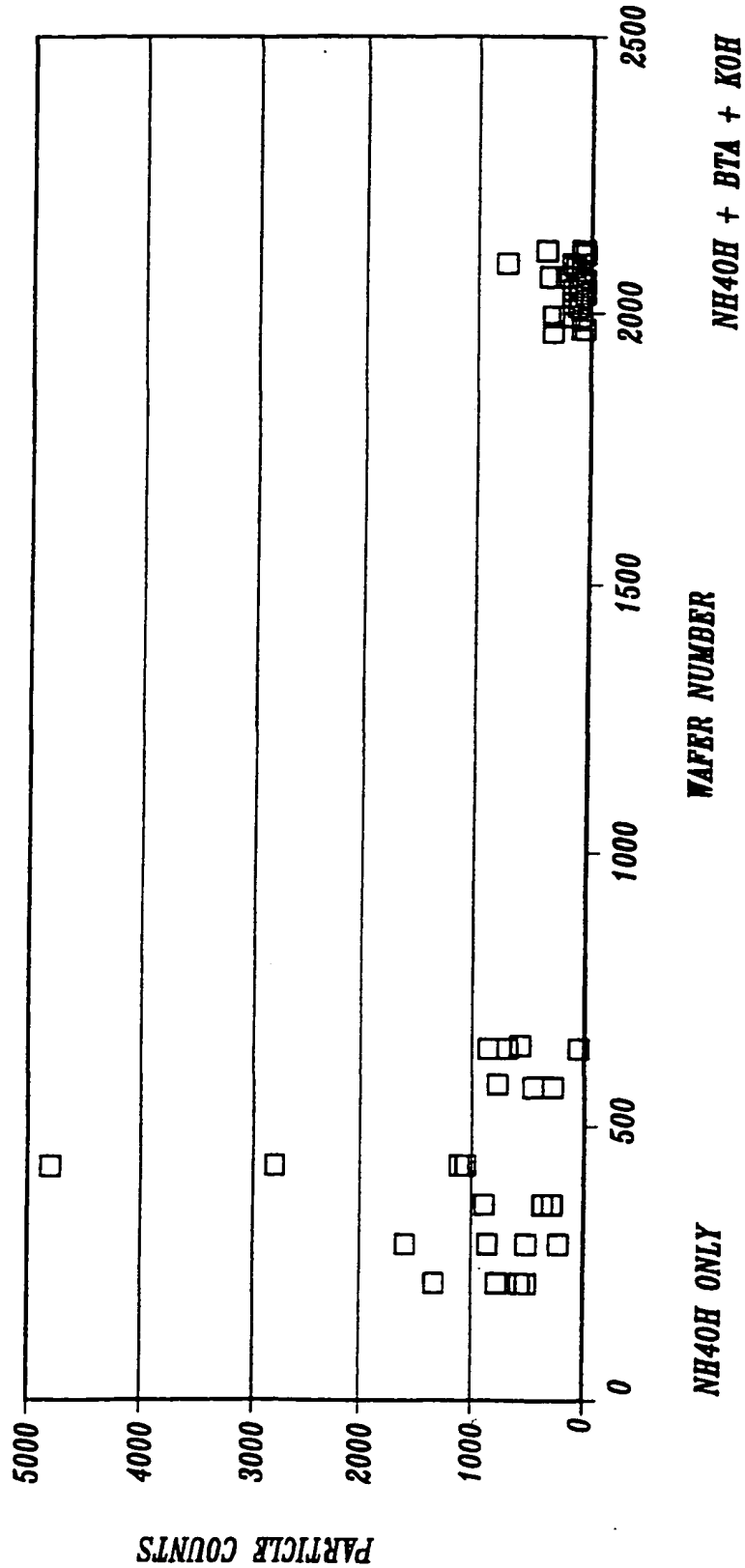


Fig. 2.

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/01965

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01L21/306 H01L21/3213

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L 603F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>LUO Q ET AL: "Chemical-mechanical polishing of copper in alkaline media" THIN SOLID FILMS, CH, ELSEVIER-SEQUOIA S.A. LAUSANNE, vol. 311, no. 1-2, 31 December 1997 (1997-12-31), pages 177-182, XP004121339 ISSN: 0040-6090 page 181, column 2; table 2</p> <p style="text-align: center;">-/-</p>	1-12



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents:

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Date of the actual completion of the international search

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Form PCT/ISA/210 (second sheet) (July 1992)

Authorized officer

Szarowski, A

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DOBROVOL'SKAYA V.P., NEZNAMOVA T.G., BARANNIK V.P.: "Inhibiting action of benzotriazole, mercaptobenzothiazole, acetanilide, cupron, oxine, and thiooxine in ammonia and in caustic soda in presence of ammonium ions" SEVASTOPOL' INSTITUTE OF INSTRUMENT CONSTRUCTION, 1967, pages 1771-1773, XP000914178 translated from Zhurnal Prikladnoi Khimii, Vol. 40, No. 8, pp. 1841-1843, August, 1967. the whole document</p>	1-6
P, X	<p>WO 99 44101 A (ALPHA METALS) 2 September 1999 (1999-09-02) example 1</p>	1, 7
A	<p>US 5 489 557 A (JOLLEY MICHAEL K) 6 February 1996 (1996-02-06) abstract</p>	

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Information on patent family members

Int. .onal Application No

PCT/US 00/01965

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9944101	A	02-09-1999	NONE	
US 5489557	A	06-02-1996	AU 7221294 A WO 9504372 A	28-02-1995 09-02-1995